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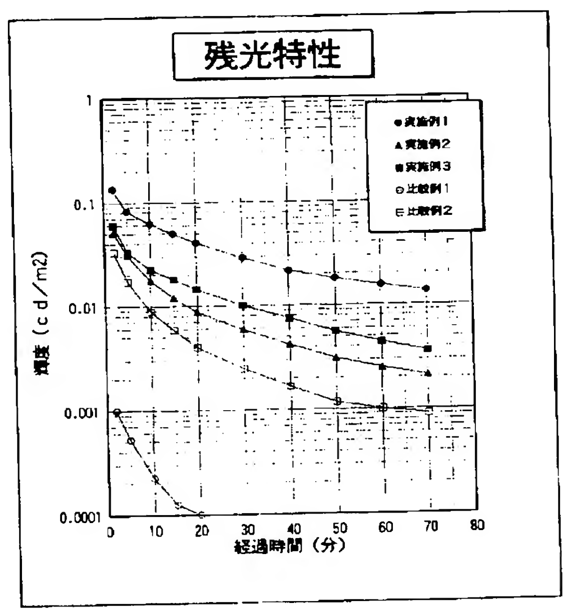
(54)【発明の名称】　蓄光性蛍光体

(57)【要約】

【課題】　市販のＺｎＳ：Ｃｕ黄緑色蓄光性発光蛍光体に比べても、はるかに長い残光特性を有し、青色から緑色発光及び残光特性を有し、化学的に安定で耐候性に優れた蓄光性蛍光体を提供しようとするものである。

【解決手段】　$m(Sr_{1-a}M^1{}_a)O \cdot n(Mg_{1-b}M^2{}_b)O \cdot 2(Si_{1-c}Ge_c)O_2:Eu_x\,Ln_y$ で表され、式中M^1はCa, Ba 、M^2はBe, Zn, Cd、LnはSc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr, Mnを示し、式中a, b, c, m, n, x, y は下記の範囲にあり、かつ、F, Cl, Br, I 等のハロゲン元素を1×10^{-5}～1×10^{-1}ｇ・ａｔｍ／母体１モルの範囲で含有する蓄光性蛍光体である。

$0\leqq a\leqq0.8$ 、$0\leqq b\leqq0.2$ 、$0\leqq c\leqq0.2$ 、$1.5\leqq m\leqq2.5$ 、$0.5\leqq m\leqq1.5$、$1\times10^{-5}\leqq x\leqq1\times10^{-1}$、$1\times10^{-5}\leqq y\leqq1\times10^{-1}$



【特許請求の範囲】

【請求項１】　Ｅｕ付活珪酸塩蓄光性蛍光体において、組成式ｍ（$Sr_{1-a}M^1{}_a$）Ｏ・ｎ（$Mg_{1-b}M^2{}_b$）Ｏ・２（$Si_{1-c}Ge_c$）O_2 ：$Eu_x\,Ln_y$ で表され、式中M^1 はＣａ及びＢａから選択された一種以上の元素、M^2 はＢｅ，Ｚｎ及びＣｄから選択された一種以上の元素、共付活剤ＬｎはＳｃ，Ｙ，Ｌａ，Ｃｅ，Ｐｒ，Ｎｄ，Ｓｍ，Ｇｄ，Ｔｂ，Ｄｙ，Ｈｏ，Ｅｒ，Ｔｍ，Ｙｂ，Ｌｕ，Ｂ，Ａｌ，Ｇａ，Ｉｎ，Ｔｌ，Ｓｂ，Ｂｉ，Ａｓ，Ｐ，Ｓｎ，Ｐｂ，Ｔｉ，Ｚｒ，Ｈｆ，Ｖ，Ｎｂ，Ｔａ，Ｍｏ，Ｗ，Ｃｒ及びＭｎから選択された一種以上の元素を示し、式中ａ，ｂ，ｃ，ｍ，ｎ，ｘ及びｙは下記の範囲にあり、かつ、前記蛍光体はＦ，Ｃｌ，Ｂｒ及びＩから選択された一種以上のハロゲン元素を、1×10^{-5}～1×10^{-1}ｇ・ａｔｍ／母体１モルの範囲で含有することを特徴とする蓄光性蛍光体。

$0 \leqq a \leqq 0.8$

$0 \leqq b \leqq 0.2$

$0 \leqq c \leqq 0.2$

$1.5 \leqq m \leqq 2.5$

$0.5 \leqq n \leqq 1.5$

$1\times10^{-5} \leqq x \leqq 1\times10^{-1}$

$1\times10^{-5} \leqq y \leqq 1\times10^{-1}$

【請求項２】　前記共付活剤ＬｎがＤｙ，Ｎｄ，Ｔｍ，Ｓｎ，Ｉｎ及びＢｉから選択された一種以上の元素であることを特徴とする請求項１記載の蓄光性蛍光体

【請求項３】　１４０～４５０ｎｍの範囲の紫外線及び／又は可視光による励起後加熱昇温するときに、少なくとも室温以上おいてに熱蛍光を呈することを特徴とする請求項１又は２記載の蓄光性蛍光体

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、屋内や屋外、さらに水中などの暗所における表示や、光源として利用することができ、耐候性に優れ、長残光性を有し、紫外線及び／又は可視光線の励起によって青色から緑色発光を呈するユーロピウム主付活の珪酸塩系の蓄光性蛍光体に関する。

【０００２】

【従来の技術】蓄光性蛍光体は、蛍光体に何らかの励起を与えて発光させた後、励起を停止した後も発光を持続する蛍光体である。ところで、蓄光性蛍光体は、表示の多様化、高機能化に伴い、蓄光性蛍光体の多色化、長残光化及び耐候性改良が求められている。従来の蓄光性蛍光体は、発光・残光の色の種類が限定され、かつ、耐候性が悪く、残光時間が短いものであった。

【０００３】ところで、青色発光蓄光性蛍光体としては、（Ｃａ，Ｓｒ）Ｓ：Ｂｉ蛍光体、黄緑色発光蓄光性蛍光体としては、ＺｎＳ：Ｃｕ蛍光体、また、赤色発光蓄光性蛍光体としては（Ｚｎ，Ｃｄ）Ｓ：Ｃｕ蛍光体が知られている。

【０００４】しかし、上記（Ｃａ，Ｓｒ）Ｓ：Ｂｉ蛍光体は、母体の化学安定性が極めて悪く、また、輝度及び残光特性も十分でないため、現在ではほとんど使用されていない。また、（Ｚｎ，Ｃｄ）Ｓ：Ｃｕ蛍光体は、毒性物質であるＣｄが母体の半分ほど占めており、輝度及び残光特性も満足できないため、現在ではほとんど使用されていない。ＺｎＳ：Ｃｕも湿気の存在下で紫外線により分解し、黒化しやすく、残光特性も不満であるが、安価なこともあり、時計の文字盤や避難誘導標識等屋内用に多用されている。

【０００５】

【発明が解決しようとする課題】本発明は、上記の欠点を解消し、長残光特性を有し、青色から緑色発光を有し、さらに化学的に安定で耐候性に優れた蓄光性蛍光体を提供しようとするものである。

【０００６】

【課題を解決するための手段】即ち、本発明は、下記の構成からなる青色から緑色発光蓄光性蛍光体である。

(1) Ｅｕ付活珪酸塩蓄光性蛍光体において、組成式ｍ（$Sr_{1-a}M^1{}_a$）Ｏ・ｎ（$Mg_{1-b}M^2{}_b$）Ｏ・２（$Si_{1-c}Ge_c$）O_2 ：$Eu_x\,Ln_y$ で表され、式中、M^1 はＣａ及びＢａから選択された一種以上の元素、M^2 はＢｅ，Ｚｎ及びＣｄから選択された一種以上の元素、共付活剤ＬｎはＳｃ，Ｙ，Ｌａ，Ｃｅ，Ｐｒ，Ｎｄ，Ｓｍ，Ｇｄ，Ｔｂ，Ｄｙ，Ｈｏ，Ｅｒ，Ｔｍ，Ｙｂ，Ｌｕ，Ｂ，Ａｌ，Ｇａ，Ｉｎ，Ｔｌ，Ｓｂ，Ｂｉ，Ａｓ，Ｐ，Ｓｎ，Ｐｂ，Ｔｉ，Ｚｒ，Ｈｆ，Ｖ，Ｎｂ，Ｔａ，Ｍｏ，Ｗ，Ｃｒ及びＭｎから選択された一種以上の元素を示し、式中ａ，ｂ，ｃ，ｍ，ｎ，ｘ及びｙは下記の範囲にあり、かつ、前記蛍光体は、Ｆ，Ｃｌ，Ｂｒ及びＩから選択された一種以上のハロゲン元素を1×10^{-5}～1×10^{-1}ｇ・ａｔｍ／母体１モルの範囲で含有することを特徴とする蓄光性蛍光体。

$0 \leqq a \leqq 0.8$

$0 \leqq b \leqq 0.2$

$0 \leqq c \leqq 0.2$

$1.5 \leqq m \leqq 2.5$

$0.5 \leqq n \leqq 1.5$

$1\times10^{-5} \leqq x \leqq 1\times10^{-1}$

$1\times10^{-5} \leqq y \leqq 1\times10^{-1}$

【０００７】(2) 前記共付活剤Ｌｎが、Ｄｙ，Ｎｄ，Ｔｍ，Ｓｎ，Ｉｎ及びＢｉから選択された一種以上の元素であることを特徴とする上記(1) 記載の蓄光性蛍光体

【０００８】(3) １４０～４５０ｎｍの範囲の紫外線及び／又は可視光による励起後加熱昇温するときに、少なくとも室温以上において熱発光を呈することを特徴とする上記 (1) 又は(2) 記載の蓄光性蛍光体

【０００９】

【発明の実施の態様】本発明者等は、（Ｓｒ，M^1）Ｏ

－（Mg，M^2）O－（Si，Ge）O_2 系の蛍光体母体（M^1＝Ca，Sr，Baで、M^2＝Be，Zn，Cdである）を中心に検討を進めたところ、図１に斜線で示す領域の組成域に、長残光化に適した蛍光体母体が存在することを見出した。即ち、組成式m（Sr，M^1）O・n（Mg，M^2）O・２（Si，Ge）O_2 で表され、m，nが、１．５≦m≦２．５で、０．５≦n≦１．５の範囲が適している。

【００１０】そして、本発明では、上記の蛍光体母体に対してＥｕで付活すると共に、Ｌｎ（Ｓｃ，Ｙ，Ｌａ，Ｃｅ，Ｐｒ，Ｎｄ，Ｓｍ，Ｇｄ，Ｔｂ，Ｄｙ，Ｈｏ，Ｅｒ，Ｔｍ，Ｙｂ，Ｌｕ，Ｂ，Ａｌ，Ｇａ，Ｉｎ，Ｔｌ，Ｓｂ，Ｂｉ，Ａｓ，Ｐ，Ｓｎ，Ｐｂ，Ｔｉ，Ｚｒ，Ｈｆ，Ｖ，Ｎｂ，Ｔａ，Ｍｏ，Ｗ，Ｃｒ及びＭｎから選択された一種以上の元素）で共付活させ、かつ、ハロゲン元素（Ｆ，Ｃｌ，Ｂｒ及びＩから選択された一種以上の元素）を含有させることにより、発光センター（Ｅｕ）や含有元素の最適化に成功し、極めて長い残光特性を有し、化学的に安定で耐侯性に優れた青色から緑色発光の蓄光性蛍光体を得ることに成功した。上記の共付活剤Ｌｎの中でも、Ｄｙ，Ｎｄ，Ｔｍ，Ｓｎ，Ｉｎ及びＢｉが特に優れている。

【００１１】本発明の組成式において、Ｓｒの置換量ａ（モル）は０≦ａ≦０．８、好ましは０≦ａ≦０．４の範囲が適しており、０．８を越えて置換すると残光特性向上の効果が少なくなる。また、Ｚｎの置換量ｂ（モル）は０≦ｂ≦０．２、好ましくは０≦ｂ≦０．１の範囲が適しており、０．２を超えて置換すると残光特性向上の効果が少なくなる。ＳｉをＧｅに置換する量ｃ（モル）は０≦ｃ≦０．２、好ましは０≦ｃ≦０．１の範囲が適しており、０．２を越えると残光特性向上の効果が少なく、輝度も低下する。

【００１２】また、蛍光体の母体構成成分であるm（Sr，M^1）O、n（Mg，M^2）O及び2（Si，Ge）O_2 の組成比を決める前記m，nの値は１．５≦m≦２．５及び０．５≦n≦１．５、好ましくは１．７≦m≦２．３及び０．７≦n≦１．３の範囲が適しており、この範囲を外れると、目的以外の化合物ができたり、原料酸化物が残存するため、輝度が低下する。

【００１３】付活剤のＥｕの配合量ｘ（ｇ・ａｔｍ）は、1×10^{-5}≦ｘ≦1×10^{-1}、好ましくは1×10^{-4}≦ｘ≦5×10^{-2}の範囲が適しており、1×10^{-5}未満では発光センターが少なくなり、目的の輝度が得られない。また、1×10^{-1}を越えると濃度消光を起こし、輝度が低下すると共に残光特性も低下する。

【００１４】共付活剤元素Ｌｎの配合量ｙ（ｇ・ａｔｍ）は、1×10^{-5}≦ｙ≦1×10^{-1}、好ましくは1×10^{-4}≦ｙ≦5×10^{-2}の範囲が適しており、1×10^{-5}未満では残光特性に効果が無く、1×10^{-1}を越えると共付活剤元素により発光するため、青色から緑色の領域の発光を得ることができない。

【００１５】本発明の蛍光体に添加するハロゲン元素は、一部融剤として結晶成長と発光センター及び共付活剤元素Ｌｎの拡散に働き、輝度及び残光特性を向上させる。ハロゲン元素の添加量ｚ（ｇ・ａｔｍ）は、洗浄処理等後の分析値としての値で1×10^{-5}≦ｚ≦1×10^{-1}、好ましくは1×10^{-4}≦ｚ≦1×10^{-2}が適している。1×10^{-1}を越えると、蛍光体が焼結して粉体への処理が困難となり、1×10^{-5}を下回ると、瞬時発光輝度及び残光低下等の不都合が生ずる。

【００１６】そして、本発明の蓄光性蛍光体は、１４０～４５０ｎｍの範囲の紫外線及び／又は可視光による励起後に、該蛍光体を加熱し昇温するときに、室温以上において熱発光を呈する。

【００１７】本発明の蓄光性蛍光体は、次のようにして合成される。蛍光体原料は、母体元素Ｓｒ，M^1（M^1＝Ｃａ，Ｂａ），Ｍｇ，M^2（M^2＝Ｂｅ，Ｚｎ，Ｃｄ），Ｓｉ，Ｇｅと、付活剤Ｅｕ及び共付活剤Ｌｎは各々酸化物もしくは焼成により容易に酸化物となりうる炭酸塩、硝酸塩、塩化物などの塩の形で用いる。また、ハロゲン元素はアンモニウム塩、アルカリ金属塩又は上記構成元素（母体構成元素、付活剤元素Ｅｕ、共付活剤元素Ｌｎ）のハロゲン化合物の形で用いる。そして、上記組成式の組成範囲になるように採取し、湿式又は乾式で充分に混合する。なお、希土類原料同志は共沈で混合させてもよい。

【００１８】この混合物をアルミナルツボ等の耐熱容器に充填し、水素含有中性ガスの還元雰囲気中又は炭素還元雰囲気中で８００～１４００℃で１～１２時間で１回以上焼成する。なお、複数焼成を行うときにも、最終焼成工程は必ず還元雰囲気中で行う。この焼成物を粉砕し、弱鉱酸洗、水洗、乾燥、篩分等を行い、本発明の蓄光性蛍光体を得る。

【００１９】図２は、実施例１で合成された蓄光性蛍光体$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$の結晶構造を確認したＸ線回折図である。この蛍光体組成のうち、Ｓｒ，Ｍｇ，Ｓｉの一部を請求項に記載の範囲で他の元素に置換してもほぼ同様の結果を示した。

【００２０】図３は、実施例１の蓄光性蛍光体（曲線ａ）、実施例２で合成された蓄光性蛍光体$Sr_{1.195}Ca_{0.8}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$（曲線ｂ）、実施例３で合成された蓄光性蛍光体$Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$（曲線ｃ）に対し、３６５ｎｍ紫外線で励起したときの発光スペクトルを示したもので、それぞれの発光ピーク波長が４７０ｎｍ、５００ｎｍ、４５０ｎｍであった。これらの蛍光体組成の一部を請求項に記載の範囲で他の元素で置換してもほぼ同様の結果を示した。

【００２１】図４は、実施例１の蓄光性蛍光体を用いて、励起スペクトルの領域を測定して示したものである。励起スペクトルの領域の測定は、分光光度計の出力側の分光波長を４７０ｎｍに固定し、試料に照射する光の励起波長を変化させた時の４７０ｎｍ（出力光）の強度をプロットしたもので、縦軸は４７０ｎｍの相対発光強度、横軸はスキャンする励起光の波長を意味する。この蛍光体組成の一部を請求項に記載の範囲で他の元素で置換してもほぼ同様の結果を示した。

【００２２】図５は、実施例１の蓄光性蛍光体（発光スペクトルピーク波長４７０ｎｍ）、実施例２の蓄光性蛍光体（発光スペクトルピーク波長５００ｎｍ）、実施例３の蓄光性蛍光体（発光スペクトルピーク波長４５０ｎｍ）、比較例１の蓄光性蛍光体（$Sr_{1.995}MgSi_2O_7:Eu_{0.005}$、発光スペクトルピーク波長４７０ｎｍ）及び、比較例２の蓄光性蛍光体（ＺｎＳ：Ｃｕ、発光スペクトルピーク波長５１６ｎｍ）に対し、昼光色蛍光ランプを用いて３００ルックスで３０分間照射し、照射停止２分後の残光特性をで測定した。測定方法は、上記の記載のように、３０Ｗの昼光色蛍光ランプを試料に照射し、ランプを切った後の蛍光体の残光を視感度フィルター付き輝度計で残光の輝度を測定した。

【００２３】図５から明らかなように、発光スペクトルピーク波長４７０ｎｍの蓄光性蛍光体である実施例１は、比較例１に対して極めて顕著な残光特性を有することが分かる。また、実施例２、３の蓄光性蛍光体も、発光色は異なるが、市販品に相当する比較例２のＺｎＳ：Ｃｕ黄緑色発光蛍光体と対比しても優れた残光特性を有していることが分かる。

【００２４】図６は、実施例１～３の蓄光性蛍光体に対し、昼光色蛍光ランプ３００ルックス１５秒照射、照射停止１分後の熱発光特性（グローカーブ）を化成オプトニクス社製、ＴＬＤリーダー(KYOKKO TLD-1300改良タイプ）を用いて約８～１０℃／秒の昇温速度で測定し、その結果を示したグラフである。図６の曲線ａ～ｃから明らかなように、実施例１～３の蓄光性蛍光体は、室温以上の温度域で上記の昇温速度で昇温すると、相対熱蛍光強度が増加していることが分かる。

【００２５】本発明の蓄光性蛍光体は、上記のように極めて高輝度長残光性を示し、耐侯性に優れかつ化学的に安定なため、従来のＺｎＳ系の蓄光性蛍光体に比べても、屋内のみならず屋外用など広い用途への利用を可能にする。例えば、種々の物品の表面に塗布したり、プラスチックス、ゴム、塩化ビニール、合成樹脂又はガラス等に混合し、成型体もしくは蛍光膜として、道路標識、視認表示、装飾品、レジャー用品、時計、ＯＡ機器、教育機器、安全標識及び建築材等に利用することができる。

【００２６】

【実施例】

〔実施例１〕

$SrCO_3$	２９．５　ｇ
MgO	４．０　ｇ
SiO_2	１２．０　ｇ
Eu_2O_3	０．０９ｇ
Dy_2O_3	０．４７ｇ
NH_4Cl	２．３　ｇ

上記の原料を充分に混合し、アルミナルツボに詰めて電気炉を用い、窒素９８％水素２％の還元雰囲気中で１１５０℃で２時間焼成した。得られた焼成物を粉砕、水洗、乾燥、篩分を行って蓄光性蛍光体を得た。

【００２７】この蛍光体は、$Sr_{1.995}MgSi_2O_7:Eu_{0.005},Dy_{0.025}Cl_{0.025}$の組成を有し、図２のＸ線回折図を示し、３６５ｎｍ紫外線で励起したときの発光スペクトルは図３（曲線ａ）のとおりで、その発光ピーク波長は４７０ｎｍの青色発光蓄光性を有するものであった。また、励起スペクトルは、図４のように可視域まで広がっていた。残光特性は、図５（曲線ａ）示すように長残光を示した。また、グローカーブは図６のとおりであった。さらに、蛍光体の発光ピーク波長、残光特性（照射停止２分後と６０分後の発光強度を、ＺｎＳ：Ｃｕ黄緑色発光蓄光蛍光体を　１００％にした発光強度比）及びグローカーブのピーク温度値を表１、及び表２に記載した。

【００２８】〔実施例２〕

$SrCO_3$	１７．６　ｇ
$CaCO_3$	８．０　ｇ
MgO	４．０　ｇ
SiO_2	１２．０　ｇ
Eu_2O_3	０．０９ｇ
Dy_2O_3	０．４７ｇ
NH_4Br	３．３　ｇ

上記の原料を充分に混合し、アルミナルツボに詰めて電気炉を用い、炭素還元雰囲気中で１２００℃で２時間焼成した。得られた焼成物を粉砕、水洗、乾燥、篩分を行って蓄光性蛍光体を得た。

【００２９】この蛍光体は、$Sr_{1.195}Ca_{0.8}MgSi_2O_7:Eu_{0.005},Dy_{0.025}Br_{0.025}$の組成を有し、３６５ｎｍ紫外線で励起したときの発光スペクトルは図３（曲線ｂ）のとおりで、そのピークは５００ｎｍの緑色発光蓄光性を有するものであった。また、残光特性は、図５（曲線ｂ）示すように長残光を示した。また、グローカーブは図６（曲線ｂ）のとおりであった。さらに、蛍光体の発光ピーク波長、残光特性（照射停止２分後と６０分後の発光強度を、ＺｎＳ：Ｃｕ黄緑色発光蓄光蛍光体を１００％にした発光強度比）及びグローピーク温度値を表１、及び表２に記載した。

【００３０】〔実施例３〕

$SrCO_3$	１４．７　ｇ
$BaCO_3$	１９．７　ｇ

MgO	4．0　g
SiO_2	12．0　g
Eu_2O_3	0．09g
Dy_2O_3	0．47g
NH_4Br	2．68g

上記の原料を充分に混合し、アルミナルツボに詰めて電気炉を用い、窒素９７％水素３％還元雰囲気中で１２００℃で３間焼成した。得られた焼成物を粉砕、水洗、乾燥、篩分を行って蓄光性蛍光体を得た。

【００３１】この蛍光体は、$Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$ の組成を有し、３６５ｎｍ紫外線で励起したときの発光スペクトルは図３（曲線ｃ）のとおりで、そのピークは５００ｎｍの青緑色発光蓄光性を有するものであった。また、残光特性は、図５（曲線ｃ）示すように長残光を示した。また、グローカーブは図６（曲線ｃ）のとおりであった。さらに、蛍光体の発光ピーク値、残光特性（照射停止２分後と６０分後の発光強度を、ＺｎＳ：Ｃｕ黄緑色蓄光性蛍光体を１００％にした発光強度比）及びグローカーブのピーク温度値を表１及び、表２に記載した。

【００３２】〔実施例４～１９〕実施例１と同様の方法で表１に記載の組成を有する実施例４～１９の蓄光性蛍光体を得た。実施例４～１９の蛍光体の発光ピーク値、残光特性（照射停止２分後と６０分後の発光強度を、ＺｎＳ：Ｃｕ黄緑色発光蓄光蛍光体を１００％にした発光強度比）及びグローピーク温度値を表１、及び表２に記載した。

【００３３】〔比較例１～２〕共付活剤元素Ｌｎ及びハロゲン元素の配合を省略した以外は、実施例１と同様にして比較例１の $Sr_{1.995}MgSi_2O_7:Eu_{0.005}$ 蓄光性蛍光体を得た。また、比較例２は化成オプトニクス社製のＺｎＳ：Ｃｕ黄緑色発光蓄光性蛍光体(LC-G1)を参照試料とした。これらの蛍光体の発光ピーク波長、残光特性（照射停止２分後と６０分後の発光強度をＺｎＳ：Ｃｕ黄緑色発光蓄光性蛍光体を１００％にした発光強度比）及びグローカーブのピーク値を表１、及び表２に記載した。

【００３４】

【表１】

	化学組成式	発光ピーク (nm)	残光特性(%) 5分後	残光特性(%) 60分後	グローピーク (℃)
実1	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	480	1540	90
実2	$Sr_{1.995}Ca_{0.9}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	500	180	250	70
実3	$Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	450	195	440	100
実4	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}$	470	60	180	85
実5	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.05}$	470	870	2530	95
実6	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.03}$	470	705	1830	95
実7	$Sr_{1.97}MgSi_2O_7:Eu_{0.03}Dy_{0.025}F_{0.01}$	470	195	280	80
実8	$Sr_{1.97}MgSi_2O_7:Eu_{0.03}Dy_{0.025}Cl_{0.025}$	470	450	990	90
実9	$Sr_{1.97}MgSi_2O_7:Eu_{0.03}Dy_{0.09}Cl_{0.025}$	470	330	710	80
実10	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Nd_{0.025}Br_{0.025}$	470	75	210	70

【００３５】

【表２】

	化学組成式	発光ピーク (nm)	残光特性(%) 5分後	60分後	グローピーク (℃)
実11	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Tm_{0.025}Br_{0.025}$	470	70	200	80
実12	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}In_{0.025}Br_{0.025}$	470	45	120	75
実13	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Bi_{0.025}Br_{0.025}$	470	40	110	70
実14	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Sn_{0.025}Br_{0.025}$	470	45	110	80
実15	$Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	470	45	230	90
実16	$Sr_{1.995}Mg_{0.9}Zn_{0.1}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	525	1330	80
実17	$Sr_{1.995}MgSi_{1.96}Ge_{0.04}O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	330	1200	80
実18	$Sr_{1.995}Mg_{0.97}Cd_{0.03}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.03}$	470	420	920	75
実19	$Sr_{1.995}Mg_{0.97}Be_{0.03}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	395	900	80
比1	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}$	470	3	0	80
比2	ZnS:Cu	516	100	100	120

【００３６】

【発明の効果】本発明は、上記の構成を採用することにより、化学的に安定で、市販のＺｎＳ系黄緑色発光蓄光蛍光体と比較しても、高輝度ではるかに長い残光を示す、青色～緑色蓄光性蛍光体を初めて提供可能とし、表示の多色化多機能化に大きく寄与するものである。

【図面の簡単な説明】

【図１】本発明の蓄光性蛍光体の母体をなす（Ｓｒ，Ｍ^1）Ｏ－（Ｍｇ，Ｍ^2）Ｏ－（Ｓｉ，Ｇｅ）$_2$Ｏ系酸化物の三元状態図を示したグラフである。

【図２】実施例１で合成した蓄光性蛍光体の結晶構造を確認したＸ線回折図である。

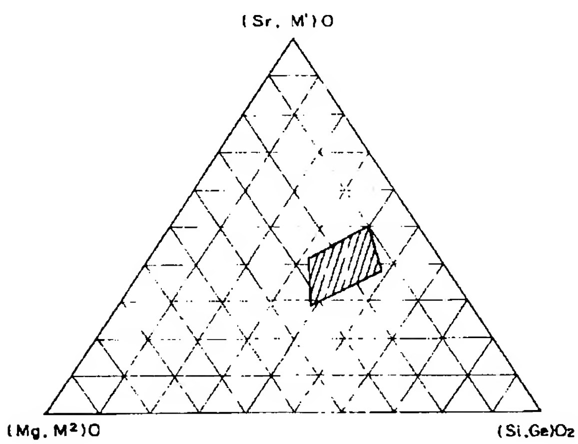
【図３】実施例１～３で合成された蓄光性蛍光体に対し、３６５ｎｍ紫外線で励起したときの発光スペクトルを示したグラフである。

【図４】実施例１の蓄光性蛍光体の各発光スペクトルピークにおける励起スペクトルを示したグラフである。

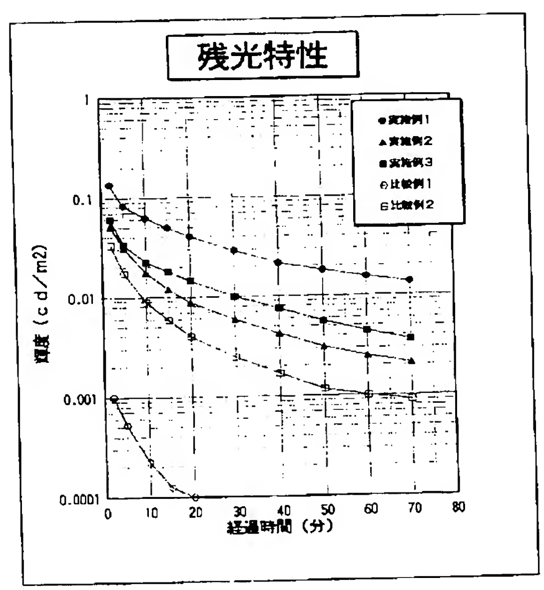
【図５】実施例１～３、及び、比較例１の青色～緑色発光蓄光性蛍光体と、比較例２の黄緑色発光蓄光性蛍光体の残光特性を比較したグラフである。

【図６】実施例１～３の蓄光性蛍光体の熱発光特性（グローカーブ）を示したグラフである。

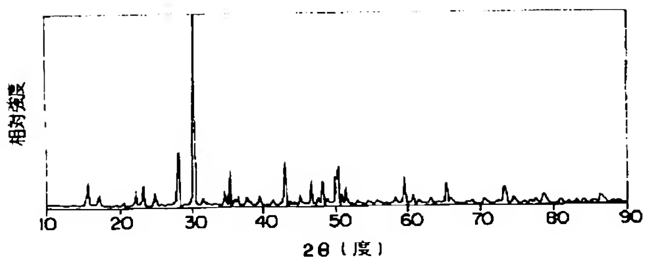
【図１】



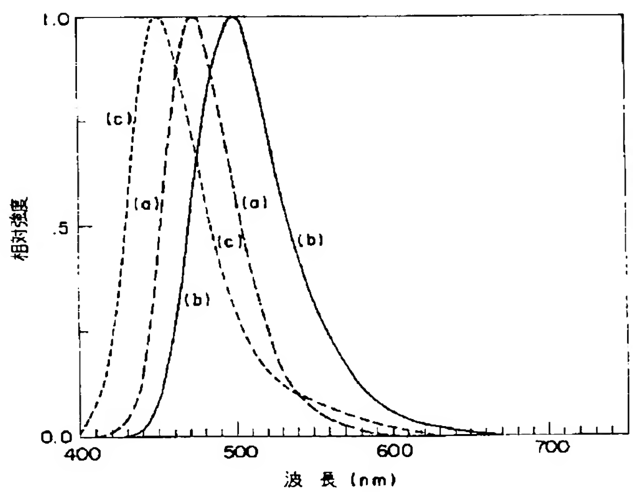
【図５】



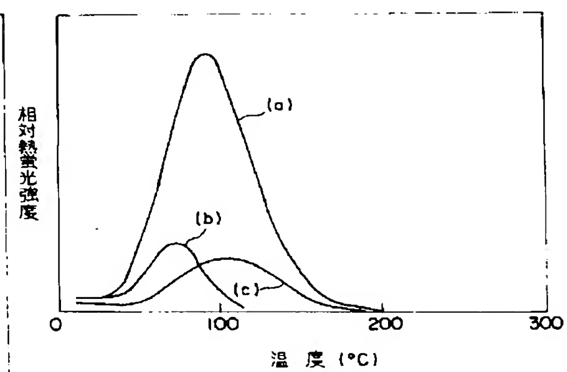
【図２】


相対強度
10
20
30
40
50
60
70
80
90
2θ（度）

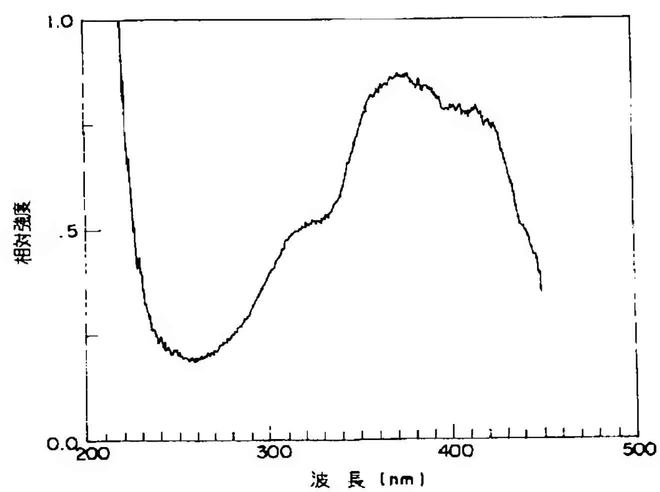
【図３】


1.0
.5
0.0
相対強度
(c)
(a)
(a)
(c)
(b)
(b)
400
500
600
700
波 長（nm）

【図６】


相対熱蛍光強度
(a)
(b)
(c)
0
100
200
300
温 度（°C）

【図４】


1.0
.5
0.0
相対強度
200
300
400
500
波 長（nm）

フロントページの続き

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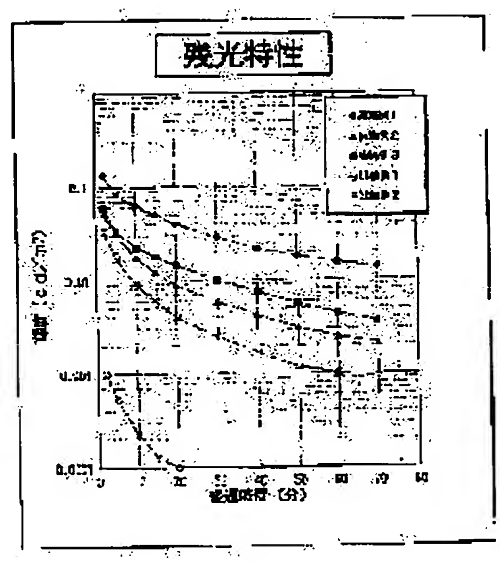
(54) PHOTOSTIMULABLE PHOSPHOR

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a photostimulable phosphor having afterglow far longer than that of commercial yellowish-green ZnS:Cu photostimulable phosphors, blue to green luminescence and afterglow, and chemical stability and excellent weather resistance.
SOLUTION: This phosphor is represented by the formula: m(Sr1-aM1a)O.n(Mg1-bM2b)O.2(Si1cGec)O2:EuxLny (wherein M1 is Ca or Ba; M2 is Be, Zn or Cd; Ln is Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr or Mn, and a, b, c, m, n, x and y are in the following ranges: 0≤a≤0.8, 0≤b≤0.2, 0≤c≤0.2, 1.5≤m≤2.5, 0.5≤m≤1.5, 1 × 10-5≤x≤1 × 10-1, and 1 × 10-5≤y≤1 × 10-1) and further contains halogen atoms (F, Cl, Br or I) in an amount in the range of 1 × 10-5 to 1 × 10-1g.atom/mol of the matrix.



CLAIMS

[Claim(s)]

[Claim 1]It is expressed with empirical formula $m(Sr_{1-a}M^1{}_a)$ O-$n(Mg_{1-b}M^2{}_b)$ O and $2(Si_{1-c}germanium_c)O_2$:$Eu_xLn_y$ in Eu activation silicate phosphorescent materials, An element more than a kind as which $M^{1 in\ formula}$ was chosen from Ca and Ba, an element more than a kind as which M^2 was chosen from Be, Zn, and Cd, The co-activating agent Ln Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, aluminum, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr. And an element more than a kind chosen from Mn is shown, and the inside a, b, and c of a formula, m, n, x, and y are in the following range, And phosphorescent materials, wherein said fluorescent substance contains a halogen more than a kind chosen from F, Cl, Br, and I in the range of 1 mol of $1x10^{-5}$ - $1x10^{-1}$g-atm / parents.

0 <=a<= 0.80 <=b<= 0.20 <=c<= 0.21.5 <=m<= 2.50.5 <=n<=1.51x10^{-5}<=x<= 1x10^{-1}1x10^{-5}<=y<= 1x10^{-1}[Claim 2]The phosphorescent materials according to claim 1 being the elements more than a kind as which said co-activating agent Ln was chosen from Dy, Nd, Tm, Sn, In, and Bi [Claim 3]when [at which it is based on ultraviolet rays and/or visible light of the range of 140-450 nm] carrying out excitation afterbaking temperature up, beyond a room temperature sets at least — ** — the phosphorescent materials according to claim 1 or 2 presenting heat fluorescence

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention can be used as indoor, the outdoors, a display [in / further / dark places, such as underwater,], and a light source, is excellent in weatherability, has high-persistence, and relates to the phosphorescent materials of a silicate system of the europium main activation which presents green emission from blue by excitation of ultraviolet rays and/or visible light.
[0002]
[Description of the Prior Art]Phosphorescent materials are fluorescent substances which maintain luminescence, even after making a certain excitation give and emit light to a fluorescent substance, and suspending excitation. By the way, as for phosphorescent materials, multiple-color-izing of phosphorescent materials, long-afterglow-izing, and weatherability improvement are called for with diversification of a display, and advanced features. The kind of color of luminescence and an afterglow was limited, and the conventional phosphorescent materials had bad weatherability, and its afterglow time was short.
[0003]By the way, as blue light phosphorescent materials, the S:Cu (Zn, Cd) fluorescent substance is known as a ZnS:Cu fluorescent substance and red light phosphorescent materials as a S:Bi (Ca, Sr) fluorescent substance and yellowish green luminescence phosphorescent materials.
[0004]However, since the chemical stability of a parent is very bad and luminosity and a persistence characteristic do not have it, either, the above-mentioned (Ca, Sr) S:Bi fluorescent substance is hardly used now. [enough] Cd whose S:Cu (Zn, Cd) fluorescent substance is a toxic substance occupies the half of the parent.
Since luminosity and a persistence characteristic are also unsatisfying, it is hardly used now.
Ultraviolet rays decompose and it is easy to carry out melanism also of ZnS:Cu under existence of humidity, and although a persistence characteristic is also dissatisfied, since it is cheap, it is used abundantly at indoor types, such as a dial face, an escape guide sign, etc. of a clock.
[0005]
[Problem(s) to be Solved by the Invention]This invention cancels the above-mentioned fault, has the long afterglow characteristic, has green emission from blue, is still more chemically stable and tends to provide phosphorescent materials excellent in weatherability.
[0006]
[Means for Solving the Problem]That is, this invention is the green emission phosphorescent materials from blue which consists of the following composition.
(1) It is expressed with empirical formula $m(Sr_{1-a}M^1{}_a)$ O-$n(Mg_{1-b}M^2{}_b)$ O and $2(Si_{1-c}germanium_c)O_2$:$Eu_xLn_y$ in Eu activation silicate phosphorescent materials, An element more than a kind as which M^1 was chosen from Ca and Ba among a formula, an element more than a kind as which M^2 was chosen from Be, Zn, and Cd, The co-activating agent Ln Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, aluminum, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr. And an element more than a kind chosen from Mn is shown, and the inside a, b, and c of a formula, m, n, x, and y are in the following range, and and said fluorescent substance, Phosphorescent materials containing a halogen more than a kind chosen from F, Cl, Br, and I in the range of 1 mol of $1x10^{-5}$ - $1x10^{-1}$g-atm / parents.
0 <=a<= 0.80 <=b<= 0.20 <=c<= 0.21.5 <=m<= 2.50.5 <=n<=1.51x10^{-5}<=x<= 1x10^{-1}1x10^{-5}<=y<= 1x10^{-1}[0007](2) Phosphorescent materials given in above-mentioned (1), wherein said co-activating agent Ln is an element more than a kind chosen from Dy, Nd, Tm, Sn, In, and Bi [0008](3) Phosphorescent materials the above-mentioned (1) or given in (2) characterized by presenting thermoluminescence at least beyond a room temperature when [at which it is based on ultraviolet rays and/or visible light of the range of 140-450 nm] carrying out excitation afterbaking temperature up
[0009]
[A mode of implementation of an invention] This invention persons are the fluorescent substance parents (it is M^1=Ca, Sr, and Ba and) of an O(Sr, M^1)-(Mg, M^2) O-(Si, germanium) O_2 system. M^2=Be, Zn, and Cd -- it is -- when examination was advanced to a center, it found out that a fluorescent substance parent suitable for long afterglow-ization existed in a presentation region of a field shown in drawing 1 with a slash. That is, it is expressed with empirical formula m(Sr, M^1) O-n(Mg, M^2) O and 2(Si, germanium)O_2, and the range of 0.5<=n<=1.5 is suitable for m and n by 1.5<=m<=2.5.
[0010]And in this invention, activate with Eu to the above-mentioned fluorescent substance parent, and. Ln (Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, aluminum, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, and W -- Cr.) And by making it coactivate by an element more than a kind chosen from Mn, and making a halogen (element more than a kind chosen from F, Cl, Br, and I) contain, It succeeded in optimization of a luminescence center (Eu) and a content element, and it had a very long persistence characteristic, and it was chemically stable and succeeded in obtaining phosphorescent materials of green emission from blue excellent in weatherability. Also in the above-mentioned co-activating agent Ln, Dy, Nd, Tm, Sn, In, and especially Bi are excellent.
[0011]in an empirical formula of this invention -- the amount a of substitution of Sr (mol) -- 0<=a<=0.8 -- good -- better -- the range of ** 0<=a<=0.4 is suitable, and if it replaces exceeding 0.8, an effect of improvement in a persistence characteristic will decrease. the amount b of substitution of Zn (mol) -- 0<=b<=0.2 -- the range of

0<=b<=0.1 is preferably suitable, and if it replaces exceeding 0.2, an effect of improvement in a persistence characteristic will decrease. the quantity c (mol) which replaces Si by germanium -- 0<=c<=0.2 -- good -- better -- the range of ** 0<=c<=0.1 is suitable, if 0.2 is exceeded, there will be few effects of improvement in a persistence characteristic, and luminosity will also fall.

[0012]m(Sr, M^1) O which is a parent constituent of a fluorescent substance, a value of said m which determines composition ratio of n(Mg, M^2) O and 2(Si, germanium)O_2, and n -- 1.5<=m<=2.5 and 0.5<=n<=1.5 -- the range of 1.7<=m<=2.3 and 0.7<=n<=1.3 being preferably suitable, and, Since compounds other than the purpose are made or a material oxide remains if it separates from this range, luminosity falls.

[0013]the loadings x of Eu of an activator (g-atm) -- $1x10^{-5}$<=x<=$1x10^{-1}$ -- the range of $1x10^{-4}$<=x<=$5x10^{-2}$ is preferably suitable, by less than $1x10^{-5}$, a luminescence center decreases and the target luminosity is not obtained. If $1x10^{-1}$ is exceeded, will start concentration quenching and luminosity will fall, and a persistence characteristic also falls.

[0014]The loadings y of the co-activating agent element Ln (g-atm). $1x10^{-5}$<=y<=$1x10^{-1}$ -- the range of $1x10^{-4}$<=y<=$5x10^{-2}$ being preferably suitable, and, By less than $1x10^{-5}$, there is no effect in a persistence characteristic, and since light will be emitted with a co-activating agent element if $1x10^{-1}$ is exceeded, luminescence of a green field cannot be obtained from blue.

[0015]Some halogens added to a fluorescent substance of this invention work as a fusing agent to diffusion of crystal growth, a luminescence center, and the co-activating agent element Ln, and raise luminosity and a persistence characteristic. the addition z of a halogen (g-atm) -- a value as an analytical value of the back, such as washing processing, -- $1x10^{-5}$<=z<=$1x10^{-1}$ -- $1x10^{-4}$<=z<=$1x10^{-2}$ is preferably suitable. If less [if $1x10^{-1}$ is exceeded, a fluorescent substance will sinter and processing to a granular material will become difficult, and] than $1x10^{-5}$, inconvenience, such as instant light emitting luminance and an afterglow fall, will arise.

[0016]And after excitation by ultraviolet rays and/or visible light of the range of 140-450 nm, phosphorescent materials of this invention present thermoluminescence beyond a room temperature, when heating and carrying out temperature up of this fluorescent substance.

[0017]Phosphorescent materials of this invention are compounded as follows. Parent element Sr, M^1 (M^1=Ca, Ba), Mg, M^2 (M^2=Be, Zn, Cd), Si, germanium, and activator Eu and the co-activating agent Ln use a fluorescent substance raw material in a form of salts, such as carbonate, a nitrate, a chloride, etc. which can turn into an oxide easily by an oxide or calcination respectively. A halogen is used in a form of a halogenated compound of ammonium salt, alkali metal salt, or the above-mentioned composing element (a parent composing element, activator element Eu, co-activating agent element Ln). And it extracts so that it may become a composition range of the above-mentioned empirical formula, and it fully mixes by a wet type or dry type. A rare earth raw material comrade may make it mix by coprecipitation.

[0018]Heat-resistant containers, such as an alumina crucible, are filled up with this mixture, and it is calcinated once or more at 800-1400 ** in 1 to 12 hours in reducing atmosphere of hydrogen content inert gas, or carbon reduction atmosphere. Also when performing two or more calcination, the last baking process is certainly performed in reducing atmosphere. This fired material is ground, weak ore pickling, rinsing, desiccation, screen analysis, etc. are performed, and phosphorescent materials of this invention are obtained.

[0019]Drawing 2 is the X diffraction figure which checked a crystal structure of phosphorescent-materials $Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$ compounded in Example 1. Even if it replaced a part of Sr, Mg, and Si by other elements in the range given in a claim among this fluorescent substance presentation, almost same result was shown.

[0020]Phosphorescent-materials $Sr_{1.195}Ca_{0.8}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$ by which drawing 3 was compounded in phosphorescent materials (curve a) of Example 1, and Example 2 (curve b), As opposed to phosphorescent-materials $Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$ (curve c) compounded in Example 3, It was what showed an emission spectrum when excited by 365-nm ultraviolet rays, and each emission peak wavelength was 470 nm, 500 nm, and 450 nm. Even if other elements replaced a part of these fluorescent substance presentations with a claim in the range of a statement, almost same result was shown.

[0021]Drawing 4 measures and shows a field of an excitation spectrum using phosphorescent materials of Example 1. Measurement of a field of an excitation spectrum fixes spectrum wavelength of an output side of a spectrophotometer to 470 nm, it is what plotted intensity of 470 nm (outputted ray) when excited wavelengths of light irradiate a sample were changed, and a vertical axis means wavelength of excitation light which scans relative luminescence intensity of 470 nm, and a horizontal axis. Even if other elements replaced a part of this fluorescent substance presentation with a claim in the range of a statement, almost same result was shown.

[0022]Drawing 5 Phosphorescent materials of Example 1 (luminescence spectral peak wavelength of 470 nm), Phosphorescent materials of Example 2 (luminescence spectral peak wavelength of 500 nm), Phosphorescent materials of Example 3 (luminescence spectral peak wavelength of 450 nm), phosphorescent materials ($Sr_{1.995}MgSi_2O_7:Eu_{0.005}$.) of the comparative example 1 to luminescence spectral peak wavelength of 470 nm, and phosphorescent materials (ZnS:Cu, luminescence spectral peak wavelength of 516 nm) of the comparative example 2, it glared for 30 minutes at 300 luxs using a daylight fluorescent lamp, and a persistence characteristic 2 minutes after an exposure stop was come out of and measured. Like the above-mentioned statement, a measuring method irradiated a sample with a daylight fluorescent lamp of 30W, and measured luminosity of an afterglow for an afterglow of a fluorescent substance after turning off the lamp with a luminance meter with a spectral-luminous-efficacy filter.

[0023]It turns out that Example 1 which is phosphorescent materials with a luminescence spectral peak wavelength of 470 nm has a very remarkable persistence characteristic to the comparative example 1 so that clearly from drawing 5. It turns out that it has the persistence characteristic which was excellent even if it contrasted them with a ZnS:Cu yellowish green luminescence fluorescent substance of the comparative example 2 equivalent to a commercial item, although phosphorescent materials of Examples 2 and 3 also differed in the luminescent color.

[0024]Drawing 6 to phosphorescent materials of Examples 1-3 A daylight-fluorescent-lamp 300 lux 15-second exposure, It is the graph which measured the thermoluminescence characteristic (glow curve) 1 minute after an exposure stop with a heating rate of about 8-10 **/second using the Kasei Optonix, Ltd. make and a TLD leader (KYOKKO TLD-1300 improvement type), and showed the result. When temperature up of the phosphorescent materials

of Examples 1-3 is carried out with the above-mentioned heating rate in a temperature region beyond a room temperature so that clearly from curvilinear a-c of drawing 6, it turns out that relative heat fluorescence intensity is increasing.
[0025]Since phosphorescent materials of this invention show high-intensity high-persistence extremely as mentioned above, and it is chemically stable, even if it excels in weatherability, and they compare it with phosphorescent materials of the conventional ZnS system, they enable use for a large use, such as not only indoor but the outdoor type. For example, it can apply to the surface of various articles, or can mix on plastics, rubber, vinyl chloride, a synthetic resin, or glass, and can use for a road sign, a visual recognition display, accessories, leisure goods, a clock, OA equipment, educational aid, a safety sign, a building material, etc. as a molding body or a fluorescent screen.
[0026]
[Example]
[Example 1]
The raw material of the $SrCO_3$29.5 gMgO 4.0 g$SiO_2$12.0 g$Eu_2O_3$0.09g$Dy_2O_3$0.47gNH_4Cl 2.3 g above is fully mixed, The alumina crucible was stuffed and it calcinated at 1150 ** for 2 hours using the electric furnace in the reducing atmosphere of 2% of 98% of nitrogen hydrogen. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained fired material, and phosphorescent materials were obtained.
[0027]This fluorescent substance has the presentation of $Sr_{1.995}MgSi_2O_7$:$Eu_{0.005}$ and $Dy_{0.025}Cl_{0.025}$. The X diffraction figure of drawing 2 is shown, when it excites by 365-nm ultraviolet rays, an emission spectrum is as drawing 3 (curve a), and the emission peak wavelength has the blue light light storaging of 470 nm. The excitation spectrum had spread to the visible range like drawing 4. The persistence characteristic showed long afterglow so that drawing 5 (curve a) might be shown. The glow curve was as drawing 6. The emission peak wavelength of a fluorescent substance, the persistence characteristic (about the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after, it is a ZnS:Cu yellowish green luminescence light storage fluorescent substance luminescence intensity ratio made 100%), and the peak temperature value of the glow curve were indicated to Table 1 and 2.
[0028][Example 2]
The raw material of the $SrCO_3$17.6 g$CaCO_3$8.0 gMgO 4.0 g$SiO_2$12.0 g$Eu_2O_3$0.09g$Dy_2O_3$0.47gNH_4Br 3.3 g above is fully mixed, The alumina crucible was stuffed and it calcinated at 1200 ** in carbon reduction atmosphere for 2 hours using the electric furnace. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained fired material, and phosphorescent materials were obtained.
[0029]This fluorescent substance has the presentation of $Sr_{1.195}Ca_{0.8}MgSi_2O_7$:$Eu_{0.005}$ and $Dy_{0.025}Br_{0.025}$. When it excites by 365-nm ultraviolet rays, an emission spectrum is as drawing 3 (curve b), and the peak has the green emission light storaging of 500 nm. The persistence characteristic showed long afterglow so that drawing 5 (curve b) might be shown. The glow curve was as drawing 6 (curve b). The emission peak wavelength, persistence characteristic (luminescence intensity ratio which made 100% the ZnS:Cu yellowish green luminescence light storage fluorescent substance for the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after), and glow peak temperature value of the fluorescent substance were indicated to Table 1 and 2.
[0030][Example 3]
The raw material of the $SrCO_3$14.7 g$BaCO_3$19.7 gMgO 4.0 g$SiO_2$12.0 g$Eu_2O_3$0.09g$Dy_2O_3$0.47gNH_4Br 2.68g above is fully mixed, The alumina crucible was stuffed and three between was calcinated at 1200 ** using the electric furnace in 3% of 97% of nitrogen hydrogen reducing atmosphere. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained fired material, and phosphorescent materials were obtained.
[0031]This fluorescent.substance has the presentation of $Sr_{0.995}Ba_{1.0}MgSi_2O_7$:$Eu_{0.005}Dy_{0.025}Br_{0.025}$. When it excites by 365-nm ultraviolet rays, an emission spectrum is as drawing 3 (curve c), and the peak has the blue-green luminescence light storaging of 500 nm. The persistence characteristic showed long afterglow so that drawing 5 (curve c) might be shown. The glow curve was as drawing 6 (curve c). The light emission peak value of a fluorescent substance, the persistence characteristic (luminescence intensity ratio which made ZnS:Cu yellowish green phosphorescent materials 100% for the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after), and the peak temperature value of the glow curve were indicated to Table 1 and 2.
[0032][Examples 4-19] The phosphorescent materials of Example 1 and Examples 4-19 which have the presentation of a statement in Table 1 in a similar way were obtained. The light emission peak value, persistence characteristic (luminescence intensity ratio which made 100% the ZnS:Cu yellowish green luminescence light storage fluorescent substance for the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after), and glow peak temperature value of the fluorescent substance of Examples 4-19 were indicated to Table 1 and 2.
[0033][Comparative examples 1-2] The $Sr_{1.995}MgSi_2O_7$:$Eu_{0.005}$ phosphorescent materials of the comparative example 1 were obtained like Example 1 except having omitted combination of the co-activating agent element Ln and the halogen. The comparative example 2 made the reference sample the ZnS:Cu yellowish green luminescence phosphorescent materials by Kasei Optonix, Ltd. (LC-G1). The peak value of the emission peak wavelength of these fluorescent substances, the persistence characteristic (luminescence intensity ratio which made 100% ZnS:Cu yellowish green luminescence phosphorescent materials for the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after), and the glow curve was indicated to Table 1 and 2.
[0034]
[Table 1]

	化学組成式	発光ピーク (nm)	残光特性(%) 5分後	60分後	グローピーク (℃)
実1	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	480	1540	90
実2	$Sr_{1.895}Ca_{0.1}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	500	180	250	70
実3	$Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	450	195	440	100
実4	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}$	470	60	180	85
実5	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.05}$	470	870	2530	95
実6	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.03}$	470	705	1830	95
実7	$Sr_{1.97}MgSi_2O_7:Eu_{0.03}Dy_{0.025}F_{0.01}$	470	195	280	80
実8	$Sr_{1.97}MgSi_2O_7:Eu_{0.03}Dy_{0.025}Cl_{0.025}$	470	450	990	90
実9	$Sr_{1.97}MgSi_2O_7:Eu_{0.03}Dy_{0.07}Cl_{0.325}$	470	330	710	80
実10	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Nd_{0.025}Br_{0.025}$	470	75	210	70

[0035]
[Table 2]

	化学組成式	発光ピーク (nm)	残光特性(%) 5分後	60分後	グローピーク (℃)
実11	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Tm_{0.025}Br_{0.025}$	470	70	200	80
実12	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}In_{0.025}Br_{0.025}$	470	45	120	75
実13	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Bi_{0.025}Br_{0.025}$	470	40	110	70
実14	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Sn_{0.025}Br_{0.025}$	470	45	110	80
実15	$Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	470	45	230	90
実16	$Sr_{1.995}Mg_{0.9}Zn_{0.1}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	525	1330	80
実17	$Sr_{1.995}MgSi_{1.96}Ge_{0.04}O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	330	1200	80
実18	$Sr_{1.995}Mg_{0.97}Cd_{0.03}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.03}$	470	420	920	75
実19	$Sr_{1.995}Mg_{0.97}Be_{0.03}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	395	900	80
比1	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}$	470	3	0	80
比2	ZnS:Cu	516	100	100	120

[0036]
[Effect of the Invention]The above-mentioned composition is adopted in this invention.
Therefore, even if it is chemically stable and compares with a commercial ZnS system yellowish green luminescence light storage fluorescent substance, with high-intensity, offer of the blue - green phosphorescent materials which show a far long afterglow is enabled for the first time, and it contributes to multiple color-ized multi-functionalization of a display greatly.

[Translation done.]

TECHNICAL FIELD

[Industrial Application]This invention can be used as indoor, the outdoors, a display [in / further / dark places, such as underwater,], and a light source, is excellent in weatherability, has high-persistence, and relates to the phosphorescent materials of a silicate system of the europium main activation which presents green emission from blue by excitation of ultraviolet rays and/or visible light.

[Translation done.]

PRIOR ART

[Description of the Prior Art]Phosphorescent materials are fluorescent substances which maintain luminescence, even after making a certain excitation give and emit light to a fluorescent substance, and suspending excitation. By the way, as for phosphorescent materials, multiple-color-izing of phosphorescent materials, long-afterglow-izing, and weatherability improvement are called for with diversification of a display, and advanced features. The kind of color of luminescence and an afterglow was limited, and the conventional phosphorescent materials had bad weatherability, and its afterglow time was short.
[0003]By the way, as blue light phosphorescent materials, the S:Cu (Zn, Cd) fluorescent substance is known as a ZnS:Cu fluorescent substance and red light phosphorescent materials as a S:Bi (Ca, Sr) fluorescent substance and yellowish green luminescence phosphorescent materials.
[0004]However, since the chemical stability of a parent is very bad and luminosity and a persistence characteristic do not have it, either, the above-mentioned (Ca, Sr) S:Bi fluorescent substance is hardly used now. [enough] Cd whose S:Cu (Zn, Cd) fluorescent substance is a toxic substance occupies the half of the parent.
Since luminosity and a persistence characteristic are also unsatisfying, it is hardly used now.
Ultraviolet rays decompose and it is easy to carry out melanism also of ZnS:Cu under existence of humidity, and although a persistence characteristic is also dissatisfied, since it is cheap, it is used abundantly at indoor types, such as a dial face, an escape guide sign, etc. of a clock.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention]The above-mentioned composition is adopted in this invention.
Therefore, even if it is chemically stable and compares with a commercial ZnS system yellowish green luminescence light storage fluorescent substance, with high-intensity, offer of the blue - green phosphorescent materials which show a far long afterglow is enabled for the first time, and it contributes to multiple color-ized multi-functionalization of a display greatly.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]This invention cancels the above-mentioned fault, has the long afterglow characteristic, has green emission from blue, is still more chemically stable and tends to provide phosphorescent materials excellent in weatherability.

[Translation done.]

MEANS

[Means for Solving the Problem]That is, this invention is the green emission phosphorescent materials from blue which consists of the following composition.
(1) It is expressed with empirical formula $m(Sr_{1-a}M^1{}_a)$ O-$n(Mg_{1-b}M^2{}_b)$ O and $2(Si_{1-c}germanium_c)O_2:Eu_xLn_y$ in Eu activation silicate phosphorescent materials, An element more than a kind as which M^1 was chosen from Ca and Ba among a formula, an element more than a kind as which M^2 was chosen from Be, Zn, and Cd, The co-activating agent Ln Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, aluminum, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr. And an element more than a kind chosen from Mn is shown, and the inside a, b, and c of a formula, m, n, x, and y are in the following range, and and said fluorescent substance, Phosphorescent materials containing a halogen more than a kind chosen from F, Cl, Br, and I in the range of 1 mol of $1x10^{-5}$ - $1x10^{-1}$g-atm / parents.
0 <=a<= 0.80 <=b<= 0.20 <=c<= 0.21.5 <=m<= 2.50.5 <=n<=1.51x10^{-5}<=x<= 1x10^{-1}1x10^{-5}<=y<= 1x10^{-1}[0007](2) Phosphorescent materials given in above-mentioned (1), wherein said co-activating agent Ln is an element more than a kind chosen from Dy, Nd, Tm, Sn, In, and Bi [0008](3) Phosphorescent materials the above-mentioned (1) or given in (2) characterized by presenting thermoluminescence at least beyond a room temperature when [at which it is based on ultraviolet rays and/or visible light of the range of 140-450 nm] carrying out excitation afterbaking temperature up
[0009]
[A mode of implementation of an invention] This invention persons are the fluorescent substance parents (it is M^1=Ca, Sr, and Ba and) of an O(Sr, M^1)-(Mg, M^2) O-(Si, germanium) O_2 system. M^2=Be, Zn, and Cd — it is — when examination was advanced to a center, it found out that a fluorescent substance parent suitable for long afterglow-ization existed in a presentation region of a field shown in drawing 1 with a slash. That is, it is expressed with empirical formula m(Sr, M^1) O-n(Mg, M^2) O and 2(Si, germanium)O_2, and the range of 0.5<=n<=1.5 is suitable for m and n by 1.5<=m<=2.5.
[0010]And in this invention, activate with Eu to the above-mentioned fluorescent substance parent, and. Ln (Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, aluminum, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, and W — Cr.) And by making it coactivate by an element more than a kind chosen from Mn, and making a halogen (element more than a kind chosen from F, Cl, Br, and I) contain, It succeeded in optimization of a luminescence center (Eu) and a content element, and it had a very long persistence characteristic, and it was chemically stable and succeeded in obtaining phosphorescent materials of green emission from blue excellent in weatherability. Also in the above-mentioned co-activating agent Ln, Dy, Nd, Tm, Sn, In, and especially Bi are excellent.
[0011]in an empirical formula of this invention -- the amount a of substitution of Sr (mol) — 0<=a<=0.8 — good — better — the range of ** 0<=a<=0.4 is suitable, and if it replaces exceeding 0.8, an effect of improvement in a persistence characteristic will decrease. the amount b of substitution of Zn (mol) — 0<=b<=0.2 — the range of 0<=b<=0.1 is preferably suitable, and if it replaces exceeding 0.2, an effect of improvement in a persistence characteristic will decrease. the quantity c (mol) which replaces Si by germanium — 0<=c<=0.2 — good — better — the range of ** 0<=c<=0.1 is suitable, if 0.2 is exceeded, there will be few effects of improvement in a persistence characteristic, and luminosity will also fall.
[0012]m(Sr, M^1) O which is a parent constituent of a fluorescent substance, a value of said m which determines composition ratio of n(Mg, M^2) O and 2(Si, germanium)O_2, and n -- 1.5<=m<=2.5 and 0.5<=n<=1.5 — the range of 1.7<=m<=2.3 and 0.7<=n<=1.3 being preferably suitable, and, Since compounds other than the purpose are made or a material oxide remains if it separates from this range, luminosity falls.
[0013]the loadings x of Eu of an activator (g-atm) — 1x10^{-5}<=x<=1x10^{-1} — the range of 1x10^{-4}<=x<=5x10^{-2} is preferably suitable, by less than 1x10^{-5}, a luminescence center decreases and the target luminosity is not obtained. If 1x10^{-1} is exceeded, will start concentration quenching and luminosity will fall, and a persistence characteristic also falls.

[0014]The loadings y of the co-activating agent element Ln (g-atm). 1x10^{-5}<=y<=1x10^{-1} — the range of 1x10^{-4}<=y<=5x10^{-2} being preferably suitable, and, By less than 1x10^{-5}, there is no effect in a persistence characteristic, and since light will be emitted with a co-activating agent element if 1x10^{-1} is exceeded, luminescence of a green field cannot be obtained from blue.
[0015]Some halogens added to a fluorescent substance of this invention work as a fusing agent to diffusion of crystal growth, a luminescence center, and the co-activating agent element Ln, and raise luminosity and a persistence characteristic. the addition z of a halogen (g-atm) — a value as an analytical value of the back, such as washing processing, — 1x10^{-5}<=z<=1x10^{-1} — 1x10^{-4}<=z<=1x10^{-2} is preferably suitable. If less [if 1x10^{-1} is exceeded, a fluorescent substance will sinter and processing to a granular material will become difficult, and] than 1x10^{-5}, inconvenience, such as instant light emitting luminance and an afterglow fall, will arise.
[0016]And after excitation by ultraviolet rays and/or visible light of the range of 140-450 nm, phosphorescent materials of this invention present thermoluminescence beyond a room temperature, when heating and carrying out temperature up of this fluorescent substance.
[0017]Phosphorescent materials of this invention are compounded as follows. Parent element Sr, M^1 (M^1=Ca, Ba), Mg,

M^2 (M^2=Be, Zn, Cd), Si, germanium, and activator Eu and the co-activating agent Ln use a fluorescent substance raw material in a form of salts, such as carbonate, a nitrate, a chloride, etc. which can turn into an oxide easily by an oxide or calcination respectively. A halogen is used in a form of a halogenated compound of ammonium salt, alkali metal salt, or the above-mentioned composing element (a parent composing element, activator element Eu, co-activating agent element Ln). And it extracts so that it may become a composition range of the above-mentioned empirical formula, and it fully mixes by a wet type or dry type. A rare earth raw material comrade may make it mix by coprecipitation.

[0018]Heat-resistant containers, such as an alumina crucible, are filled up with this mixture, and it is calcinated once or more at 800-1400 ** in 1 to 12 hours in reducing atmosphere of hydrogen content inert gas, or carbon reduction atmosphere. Also when performing two or more calcination, the last baking process is certainly performed in reducing atmosphere. This fired material is ground, weak ore pickling, rinsing, desiccation, screen analysis, etc. are performed, and phosphorescent materials of this invention are obtained.

[0019]Drawing 2 is the X diffraction figure which checked a crystal structure of phosphorescent-materials $Sr_{1.995}MgSi_2O_7{:}Eu_{0.005}Dy_{0.025}Cl_{0.025}$ compounded in Example 1. Even if it replaced a part of Sr, Mg, and Si by other elements in the range given in a claim among this fluorescent substance presentation, almost same result was shown.

[0020]Phosphorescent-materials $Sr_{1.195}Ca_{0.8}MgSi_2O_7{:}Eu_{0.005}Dy_{0.025}Br_{0.025}$ by which drawing 3 was compounded in phosphorescent materials (curve a) of Example 1, and Example 2 (curve b), As opposed to phosphorescent-materials $Sr_{0.995}Ba_{1.0}MgSi_2O_7{:}Eu_{0.005}Dy_{0.025}Br_{0.025}$ (curve c) compounded in Example 3, It was what showed an emission spectrum when excited by 365-nm ultraviolet rays, and each emission peak wavelength was 470 nm, 500 nm, and 450 nm. Even if other elements replaced a part of these fluorescent substance presentations with a claim in the range of a statement, almost same result was shown.

[0021]Drawing 4 measures and shows a field of an excitation spectrum using phosphorescent materials of Example 1. Measurement of a field of an excitation spectrum fixes spectrum wavelength of an output side of a spectrophotometer to 470 nm, it is what plotted intensity of 470 nm (outputted ray) when excited wavelengths of light irradiate a sample were changed, and a vertical axis means wavelength of excitation light which scans relative luminescence intensity of 470 nm, and a horizontal axis. Even if other elements replaced a part of this fluorescent substance presentation with a claim in the range of a statement, almost same result was shown.

[0022]Drawing 5 Phosphorescent materials of Example 1 (luminescence spectral peak wavelength of 470 nm), Phosphorescent materials of Example 2 (luminescence spectral peak wavelength of 500 nm), Phosphorescent materials of Example 3 (luminescence spectral peak wavelength of 450 nm), phosphorescent materials ($Sr_{1.995}MgSi_2O_7{:}Eu_{0.005}$.) of the comparative example 1 to luminescence spectral peak wavelength of 470 nm, and phosphorescent materials (ZnS:Cu, luminescence spectral peak wavelength of 516 nm) of the comparative example 2, it glared for 30 minutes at 300 luxs using a daylight fluorescent lamp, and a persistence characteristic 2 minutes after an exposure stop was come out of and measured. Like the above-mentioned statement, a measuring method irradiated a sample with a daylight fluorescent lamp of 30W, and measured luminosity of an afterglow for an afterglow of a fluorescent substance after turning off the lamp with a luminance meter with a spectral-luminous-efficacy filter.

[0023]It turns out that Example 1 which is phosphorescent materials with a luminescence spectral peak wavelength of 470 nm has a very remarkable persistence characteristic to the comparative example 1 so that clearly from drawing 5. It turns out that it has the persistence characteristic which was excellent even if it contrasted them with a ZnS:Cu yellowish green luminescence fluorescent substance of the comparative example 2 equivalent to a commercial item, although phosphorescent materials of Examples 2 and 3 also differed in the luminescent color.

[0024]Drawing 6 to phosphorescent materials of Examples 1-3 A daylight-fluorescent-lamp 300 lux 15-second exposure, It is the graph which measured the thermoluminescence characteristic (glow curve) 1 minute after an exposure stop with a heating rate of about 8-10 **/second using the Kasei Optonix, Ltd. make and a TLD leader (KYOKKO TLD-1300 improvement type), and showed the result. When temperature up of the phosphorescent materials of Examples 1-3 is carried out with the above-mentioned heating rate in a temperature region beyond a room temperature so that clearly from curvilinear a-c of drawing 6, it turns out that relative heat fluorescence intensity is increasing.

[0025]Since phosphorescent materials of this invention show high-intensity high-persistence extremely as mentioned above, and it is chemically stable, even if it excels in weatherability, and they compare it with phosphorescent materials of the conventional ZnS system, they enable use for a large use, such as not only indoor but the outdoor type. For example, it can apply to the surface of various articles, or can mix on plastics, rubber, vinyl chloride, a synthetic resin, or glass, and can use for a road sign, a visual recognition display, accessories, leisure goods, a clock, OA equipment, educational aid, a safety sign, a building material, etc. as a molding body or a fluorescent screen.

[Translation done.]

EXAMPLE

[Example]
[Example 1]
The raw material of the $SrCO_3$29.5 gMgO 4.0 g$SiO_2$12.0 g$Eu_2O_3$0.09g$Dy_2O_3$0.47gNH_4Cl 2.3 g above is fully mixed, The alumina crucible was stuffed and it calcinated at 1150 ** for 2 hours using the electric furnace in the reducing atmosphere of 2% of 98% of nitrogen hydrogen. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained fired material, and phosphorescent materials were obtained.
[0027]This fluorescent substance has the presentation of $Sr_{1.995}MgSi_2O_7$:$Eu_{0.005}$ and $Dy_{0.025}Cl_{0.025}$. The X diffraction figure of drawing 2 is shown, when it excites by 365-nm ultraviolet rays, an emission spectrum is as drawing 3 (curve a), and the emission peak wavelength has the blue light light storaging of 470 nm. The excitation spectrum had spread to the visible range like drawing 4. The persistence characteristic showed long afterglow so that drawing 5 (curve a) might be shown. The glow curve was as drawing 6. The emission peak wavelength of a fluorescent substance, the persistence characteristic (about the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after, it is a ZnS:Cu yellowish green luminescence light storage fluorescent substance luminescence intensity ratio made 100%), and the peak temperature value of the glow curve were indicated to Table 1 and 2.
[0028][Example 2]
The raw material of the $SrCO_3$17.6 g$CaCO_3$8.0 gMgO 4.0 g$SiO_2$12.0 g$Eu_2O_3$0.09g$Dy_2O_3$0.47gNH_4Br 3.3 g above is fully mixed, The alumina crucible was stuffed and it calcinated at 1200 ** in carbon reduction atmosphere for 2 hours using the electric furnace. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained fired material, and phosphorescent materials were obtained.
[0029]This fluorescent substance has the presentation of $Sr_{1.195}Ca_{0.8}MgSi_2O_7$:$Eu_{0.005}$ and $Dy_{0.025}Br_{0.025}$. When it excites by 365-nm ultraviolet rays, an emission spectrum is as drawing 3 (curve b), and the peak has the green emission light storaging of 500 nm. The persistence characteristic showed long afterglow so that drawing 5 (curve b) might be shown. The glow curve was as drawing 6 (curve b). The emission peak wavelength, persistence characteristic (luminescence intensity ratio which made 100% the ZnS:Cu yellowish green luminescence light storage fluorescent substance for the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after), and glow peak temperature value of the fluorescent substance were indicated to Table 1 and 2.
[0030][Example 3]
The raw material of the $SrCO_3$14.7 g$BaCO_3$19.7 gMgO 4.0 g$SiO_2$12.0 g$Eu_2O_3$0.09g$Dy_2O_3$0.47gNH_4Br 2.68g above is fully mixed, The alumina crucible was stuffed and three between was calcinated at 1200 ** using the electric furnace in 3% of 97% of nitrogen hydrogen reducing atmosphere. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained fired material, and phosphorescent materials were obtained.
[0031]This fluorescent substance has the presentation of $Sr_{0.995}Ba_{1.0}MgSi_2O_7$:$Eu_{0.005}Dy_{0.025}Br_{0.025}$. When it excites by 365-nm ultraviolet rays, an emission spectrum is as drawing 3 (curve c), and the peak has the blue-green luminescence light storaging of 500 nm. The persistence characteristic showed long afterglow so that drawing 5 (curve c) might be shown. The glow curve was as drawing 6 (curve c). The light emission peak value of a fluorescent substance, the persistence characteristic (luminescence intensity ratio which made ZnS:Cu yellowish green phosphorescent materials 100% for the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after), and the peak temperature value of the glow curve were indicated to Table 1 and 2.
[0032][Examples 4-19] The phosphorescent materials of Example 1 and Examples 4-19 which have the presentation of a statement in Table 1 in a similar way were obtained. The light emission peak value, persistence characteristic (luminescence intensity ratio which made 100% the ZnS:Cu yellowish green luminescence light storage fluorescent substance for the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after), and glow peak temperature value of the fluorescent substance of Examples 4-19 were indicated to Table 1 and 2.
[0033][Comparative examples 1-2] The $Sr_{1.995}MgSi_2O_7$:$Eu_{0.005}$ phosphorescent materials of the comparative example 1 were obtained like Example 1 except having omitted combination of the co-activating agent element Ln and the halogen. The comparative example 2 made the reference sample the ZnS:Cu yellowish green luminescence phosphorescent materials by Kasei Optonix, Ltd. (LC-G1). The peak value of the emission peak wavelength of these fluorescent substances, the persistence characteristic (luminescence intensity ratio which made 100% ZnS:Cu yellowish green luminescence phosphorescent materials for the luminescence intensity of the 2-minute back of an exposure stop and 60 minutes after), and the glow curve was indicated to Table 1 and 2.
[0034]
[Table 1]

	化学組成式	発光ピーク (nm)	残光特性(%) 5分後	60分後	グローピーク (℃)
実1	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	480	1540	90
実2	$Sr_{1.895}Ca_{0.1}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	500	180	250	70
実3	$Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	450	195	440	100
実4	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}$	470	60	180	85
実5	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.05}$	470	870	2530	95
実6	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.03}$	470	705	1830	95
実7	$Sr_{1.97}MgSi_2O_7:Eu_{0.03}Dy_{0.025}F_{0.01}$	470	195	280	80
実8	$Sr_{1.97}MgSi_2O_7:Eu_{0.02}Dy_{0.025}Cl_{0.025}$	470	450	990	90
実9	$Sr_{1.[illegible]}MgSi_2O_7:Eu_{0.03}Dy_{0.07}Cl_{0.025}$	470	330	710	80
実10	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Nd_{0.025}Br_{0.025}$	470	75	210	70

[0035]
[Table 2]

	化学組成式	発光ピーク (nm)	残光特性(%) 5分後	60分後	グローピーク (℃)
実11	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Tm_{0.025}Br_{0.025}$	470	70	200	80
実12	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}In_{0.025}Br_{0.025}$	470	45	120	75
実13	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Bi_{0.025}Br_{0.025}$	470	40	110	70
実14	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}Sn_{0.025}Br_{0.025}$	470	45	110	80
実15	$Sr_{0.995}Ba_{1.0}MgSi_2O_7:Eu_{0.005}Dy_{0.025}Br_{0.025}$	470	45	230	90
実16	$Sr_{1.995}Mg_{0.9}Zn_{0.1}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	525	1330	80
実17	$Sr_{1.995}MgSi_{1.96}Ge_{0.04}O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	330	1200	80
実18	$Sr_{1.995}Mg_{0.97}Cd_{0.03}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.05}$	470	420	920	75
実19	$Sr_{1.995}Mg_{0.97}Be_{0.03}Si_2O_7:Eu_{0.005}Dy_{0.025}Cl_{0.025}$	470	395	900	80
比1	$Sr_{1.995}MgSi_2O_7:Eu_{0.005}$	470	3	0	80
比2	$ZnS:Cu$	516	100	100	120

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]the O-(Mg, M^2) O-(Si, germanium) $_2$O system which makes the parent of the phosphorescent materials of this invention (Sr, M^1) — it is the graph which showed the ternary phase diagram of the oxide.

[Drawing 2]It is the X diffraction figure which checked the crystal structure of the phosphorescent materials compounded in Example 1.

[Drawing 3]It is the graph which showed the emission spectrum when excited by 365-nm ultraviolet rays to the phosphorescent materials compounded in Examples 1-3.

[Drawing 4]It is the graph which showed the excitation spectrum in each luminescence spectral peak of the phosphorescent materials of Example 1.

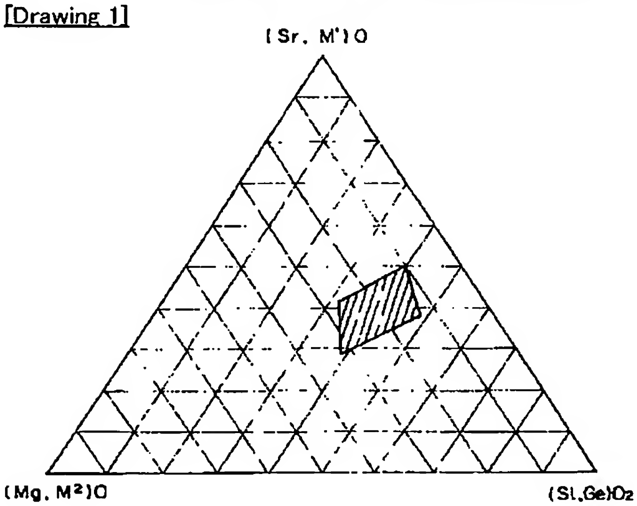
[Drawing 5]It is the graph which compared the persistence characteristic of the blue of Examples 1-3 and the comparative example 1 - green emission phosphorescent materials, and the yellowish green luminescence phosphorescent materials of the comparative example 2.

[Drawing 6]It is the graph which showed the thermoluminescence characteristic (glow curve) of the phosphorescent materials of Examples 1-3.

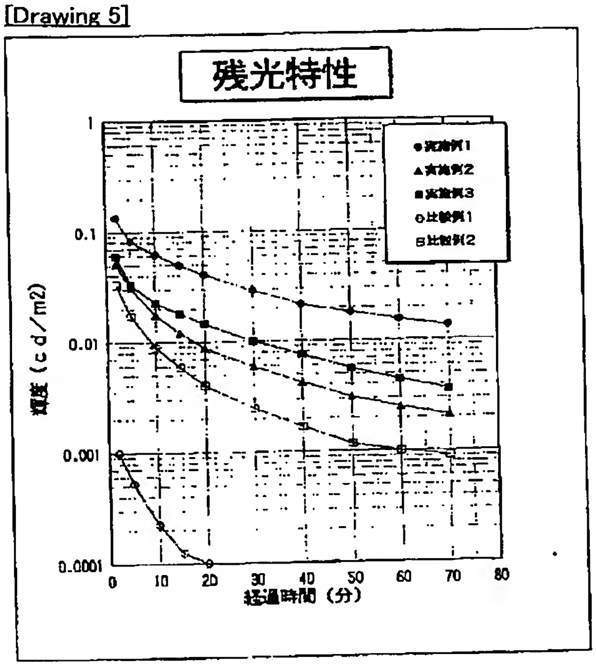
[Translation done.]

DRAWINGS

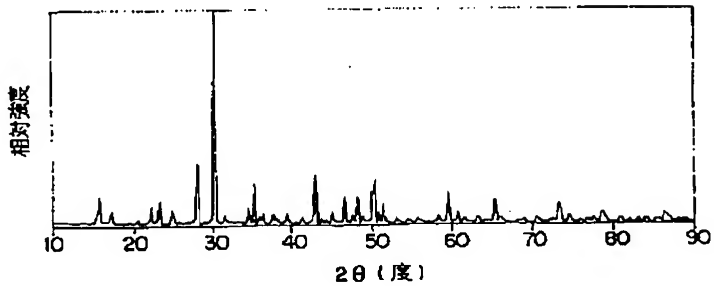
[Drawing 1]



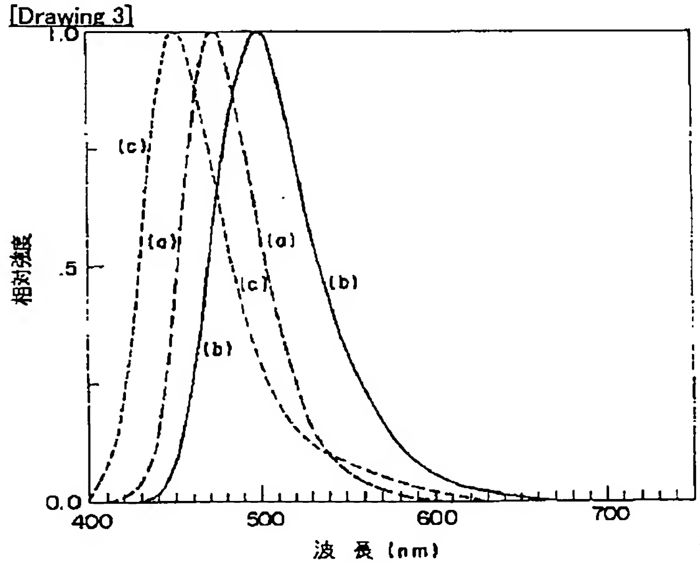
[Drawing 5]



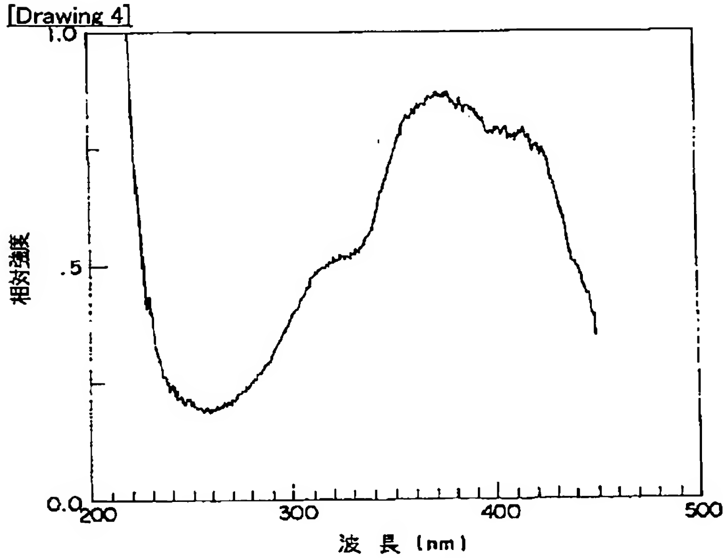
[Drawing 2]



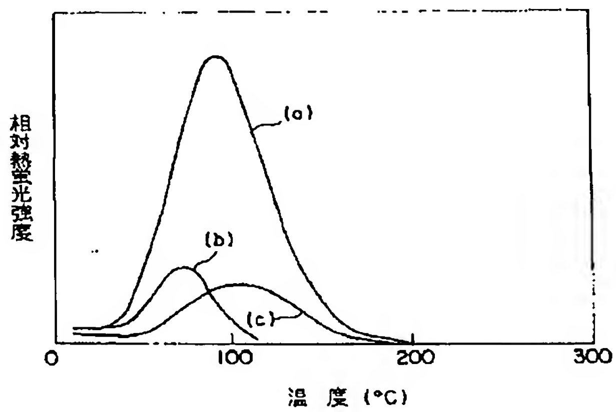
[Drawing 3]



[Drawing 4]



[Drawing 6]



[Translation done.]